(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number
WO 01/15259 A1

(51) International Patent Classification[7]: H01M 10/48, 2/36, G01R 31/36

(21) International Application Number: PCT/US00/22866

(22) International Filing Date: 18 August 2000 (18.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/378,256 20 August 1999 (20.08.1999) US

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(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

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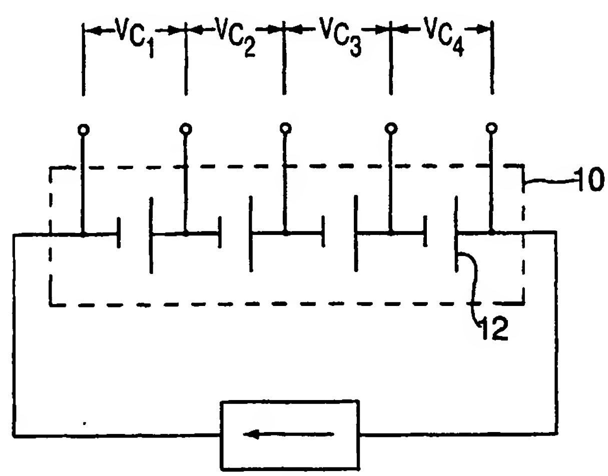
(54) Title: METHOD FOR DETERMINING AMOUNT OF WATER TO BE ADDED TO A NiCd CELL



(57) Abstract: Deficiencies in the electrolyte level of the cells (12) of NiCd battery (10) can be detected by measuring the internal resistance of the cells (12). Initially, data is collected for a battery type and capacity, correlating measured internal resistance with the amount of water that must be added to bring the cell resistance to an acceptable value. Subsequently, cells of other batteries of the same type and capacity can be measured to determine how much water must be added and the levels quickly restored. The polarization value of the cells can be used lieu of the internal resistance in the same fashion.

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Method for Determining Amount of Water to be Added to a NiCd Cell

Background of the Invention

If a cell of a nickel cadmium (NiCd) battery is overcharged, electrolysis of the water may occur, decreasing the electrolyte level in the cell. If a proper electrolyte level is not maintained, the cell will not function properly. Although the electrolyte level can be physically measured, a noninvasive, rapid technique would be highly desirable.

Brief Description of the Drawings

Figure 1 is a schematic diagram of an apparatus for determining the amount of water to be added to the cells of a storage battery;

Figure 2 is a waveform diagram of current and voltage for a cell under test; and

Figures 3-5 are drawings of the top of a battery, a battery terminal contact fixture, and a spring-loaded contact for the battery terminal contact fixture, respectively.

Summary of the Invention

The electrolyte level can be determined by observing the electrical or electrochemical behavior of the cell during a charge pulse. One method measures the internal resistance of the cells of the battery. Another method measures the polarization value of the cells. In either case, the measured quantity is correlated with an amount of water added to reduce the measured

parameter to an acceptable value and restore the electrolyte level and the electrolyte level and the performance of the cell. One aspect of this technique is the process of determining the correlation between the measured parameter and the quantities of water added. Another aspect is the use of this correlation to restore the electrolyte level.

Detailed Description of the Invention

Initially, the battery must be in a ready state. The battery, containing one or more cells, is attached to a charging system (not shown). The battery is charged for a period t at a charge rate C/ until each of the cells has an open-circuit voltage of at least v_i volts. In the case of a NiCd battery, v_i = 1.26 volts. The period t can be 15 minutes, although other values of t can be selected as suits the application. The charge rate C/ can be C/10, where C is the manufacturer's rated capacity of the battery, although the parameter can vary from greater than 1 to 100, or perhaps an even greater number, again depending on the application and the battery under test. For a battery having a capacity of 30Ah, the charge current would be 3 amps.

Utilizing the circuit of Figure 1, a battery 10 is subjected to an internal resistance test cycle. A step charge current or pulse of C amps is applied to the entire battery 10 (the value C set by the battery rating). Alternatively, a discharge pulse may be employed. The current starts at zero and goes to C instantaneously or nearly instantaneously, and is maintained at that value for a period of time, e.g., 5 seconds, after which it returns instantaneously to zero. As the step charge is applied, the battery response voltage is measured across each cell 12. The internal resistance of each cell 12 is determined by calculating

the value of dV/dI during the falling portion of the step charge pulse (see Figure 2), although one might use other portions of the pulse to measure dV/dI.

Depending on the level of electrolyte in a given cell 12, the value of dV/dI will vary. By adding water and then measuring dV/dI, the amount of water needed to return the value of cell resistance to an acceptable number can be determined. This relationship can be collected in a table or expressed as an algorithm (or depicted in a graph), as desired. Since there may be a time lag between adding water and the final value of dV/dI, one may need to perform the measurements iteratively to arrive at stabilized values of internal resistance. Following the iterative process, one would arrive at tables such as those shown below for 30Ah and 10Ah batteries for a 5 second pulse width (Tables A and B, respectively).

Water Addition Table for 30 Ah capacity-rated cells	
IR (m)	Water Addition (ml)
2.0 - 2.5	3
2.5 - 4.0	6
4.0 - 5.5	9
5.5 +	12

Table A

Water Addition Table for 10 Ah capacity-rated cells	
IR (m)	Water Addition (ml)
4.0 - 5.0	1
5.0 - 7.5	2
7.5 - 12.0	3
12.0 - 18.0	4
18.0 - 27.0	5
27.0 +	6

Table B

The tables illustrate the correlation between the measured internal resistance and the amount of water required to lower the cell resistance to an acceptable number and, thus, restore the electrolyte to its proper level. In the examples shown here, the values of acceptable maximum internal resistance, indicative of a proper electrolyte level, were selected to be 2 m and 4 m , per cell, for the respective storage batteries, although greater or lesser values could have been selected. Other pulse widths (t) and amplitudes (C) may be employed but of course will result in different table values. In these examples, the batteries utilized were manufactured by SAFT America, Inc., San Diego, CA, model no. M81757/7-2 (10 Ah) and model no. M81757/9-3 (30 Ah).

An arrangement for measuring the parameters of individual cells of a battery 100 is shown in Figures 3-5. As shown in Figure 3, the battery 100 has terminals 104 allowing direct electrical access to each of the cells 102. A battery terminal contact fixture 110, shown in Figure 4, has spring-loaded contacts 120 positioned to make contact with the terminals 104 of the

battery cells 102. The contacts 120 can have spring-loaded points 122 and positioning and tightening nuts 124 for adjusting the position of each contact 120. The contact fixture 110 has a substrate or platform 112, manufactured from a suitable insulating material, which supports the spring-loaded contacts 120. Cabling 140 (shown attached to a few exemplary contacts 120) to provide the connections illustrated in Figure 1 would be connected to the apparatus for measuring resistance (or, more correctly, dV/dI). The cabling may take the form of individual wires, a ribbon cable, or any other suitable arrangement. The current pulse may be provided using a commercially-available power supply such as a Hewlett-Packard Model No. HP-6032A power supply and the parameters may be measured using commercially-available equipment such as a National Instrument Data Acquisition Card No. AT-MIO-16XE-50.

Having generated the tables, plots, or algorithms for the battery in question, a previously untested battery can be tested to determine whether the electrolyte levels in the cells are sufficient. To run the test, the cells are again charged to at least voltage v_i and then a pulse of the proper duration is applied to the battery. The quantity dV/dI is measured for each cell and the indicated quantity of water is added to the cells as dictated by the measurements of dV/dI. The same charge current and pulse width as used to create the tables must be utilized when the test is performed to provide the proper correlation between the measured values of internal resistance and the amount of water to be added. Typically, two iterations of the pulse test, accompanied by the indicated addition of water, are sufficient to reduce the internal resistance of the battery cells to an acceptable level.

The measurements discussed above utilized a direct current pulse.

Alternatively, other devices could be used to measure the internal resistance of the cells. For example, a milliohmeter such as the Hewlett-Packard HP4338A could be employed to generate an appropriate set of tables or curves.

An alternative parameter to internal resistance is the polarization value. The polarization value is defined as the change in cell voltage, over the course of a pulse of current of constant value, divided by the amplitude of the pulse (in amps). From the polarization values, one can generate a table similar to those shown above, i.e., polarization values vs. the amount of water that must be added. When utilizing polarization value tables, care must be taken to apply pulses of the same width and magnitude as used to generate the tables.

What is claimed is:

1. A method for determining the amount of water to be added to one or more cells of a storage battery, comprising the steps of:

measuring the internal resistance or determining the polarization value, of one or more of the cells of the battery; and

adding a predetermined amount of water to the cell correlated to the internal resistance or polarization value of that cell.

2. A method as set forth in claim 1 where the step of measuring the internal resistance of a cell comprises the steps of:

passing a step charge, a pulse, or a discharge pulse of current through the cell; and

measuring the differential change in voltage across the cell.

3. A method as set forth in claim 1 where the step of determining the polarization value of a cell comprises the steps of:

passing constant current through the cell; and

measuring the change in voltage across the cell.

4. A method for determining the amount of water to be added to one or more cells of a storage battery, comprising the steps of:

measuring the internal resistance or determining the polarization value, of one or more of the cells of the battery;

adding an incremental amount of water to the cell;

repeating the two foregoing steps until the internal resistance or polarization value of that cell is reduced to an acceptable level; and

retaining the values of measured internal resistance or polarization value and the corresponding quantities of water added to the cells.

5. A method as set forth in claim 4 where the step of measuring the internal resistance of a cell comprises the steps of:

passing a step charge, a pulse, or a discharge pulse of current through the cell; and

measuring the differential change in voltage across the cell.

6. A method as set forth in claim 4 where the step of determining the polarization value of a cell comprises the steps of:

passing constant current through the cell; and

measuring the change in voltage across the cell.

7. An apparatus for determining the amount of water to be added to one or more cells of a storage battery, comprising:

means for measuring the internal resistance or determining the polarization value, of one or more of the cells of the battery; and

means for adding a predetermined amount of water to the cell correlated to the internal resistance or polarization value of that cell.

8. An apparatus as set forth in claim 7 where the means for measuring the internal resistance of a cell comprises:

means for passing a step charge, a pulse, or a discharge pulse of current through the cell; and

means for measuring the differential change in voltage across the cell.

9. An apparatus as set forth in claim 7 where the step of determining the polarization value of a cell comprises:

means for passing constant current through the cell; and

means for measuring the change in voltage across the cell.

10. An apparatus for determining the amount of water to be added to one or more cells of a storage battery, comprising:

means for measuring the internal resistance or determining the polarization value, of one or more of the cells of the battery;

means for adding an incremental amount of water to the cell;

means for repeating the two foregoing steps until the internal resistance or polarization value of that cell is reduced to an acceptable level; and

means for retaining the values of measured internal resistance or polarization value and the corresponding quantities of water added to the cells.

11. An apparatus as set forth in claim 10 where the means for measuring the internal resistance of a cell comprises:

means for passing a step charge, a pulse, or a discharge pulse of current through the cell; and

means for measuring the differential change in voltage across the cell.

12. An apparatus as set forth in claim 10 where the step of

determining the polarization value of a cell comprises:

means for passing constant current through the cell; and

means for measuring the change in voltage across the cell.

13. An apparatus for simultaneously measuring the resistance of two or more cells of a storage battery having a plurality of terminals connected to the cells, comprising:

a platform, the platform being fabricated from an insulating material;

a plurality of spring-loaded contacts, positioned in the platform to make simultaneous contact with the terminals of the battery cells and comprising spring-loaded points; and

means for connecting the terminals to a means for measuring resistance.

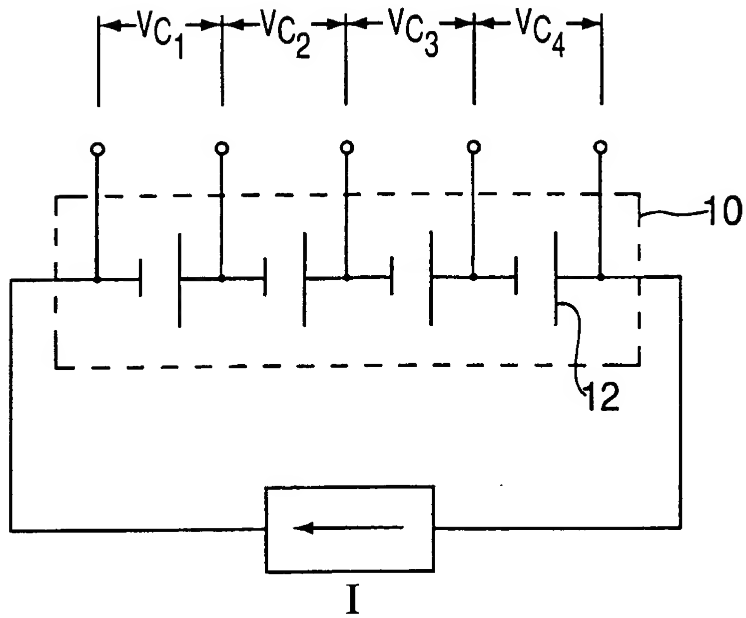

FIG. 1

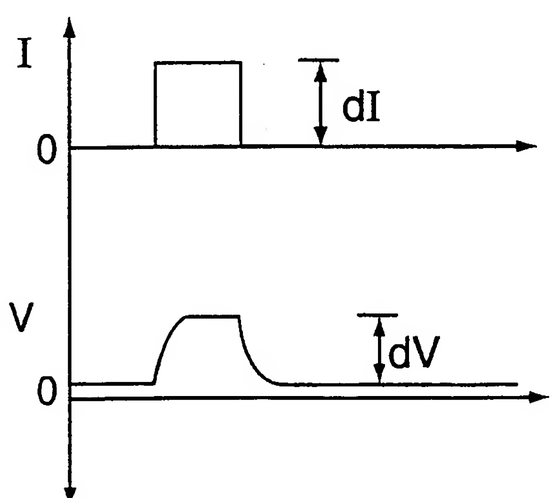

FIG. 2

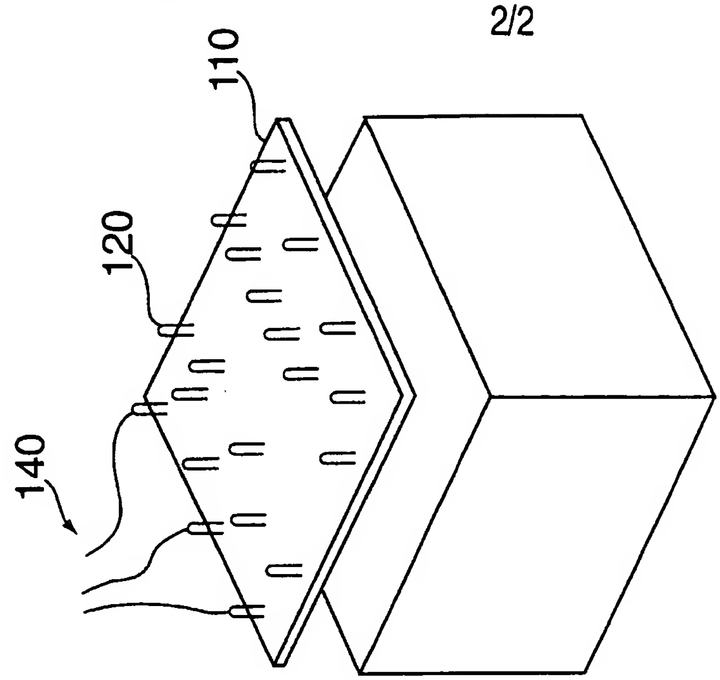

FIG. 4

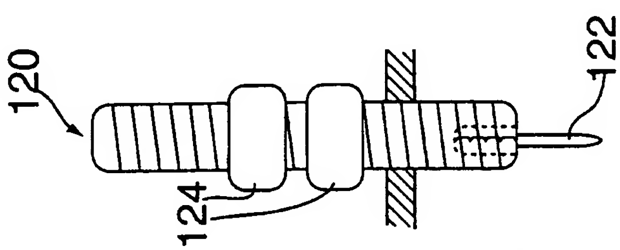

FIG. 5

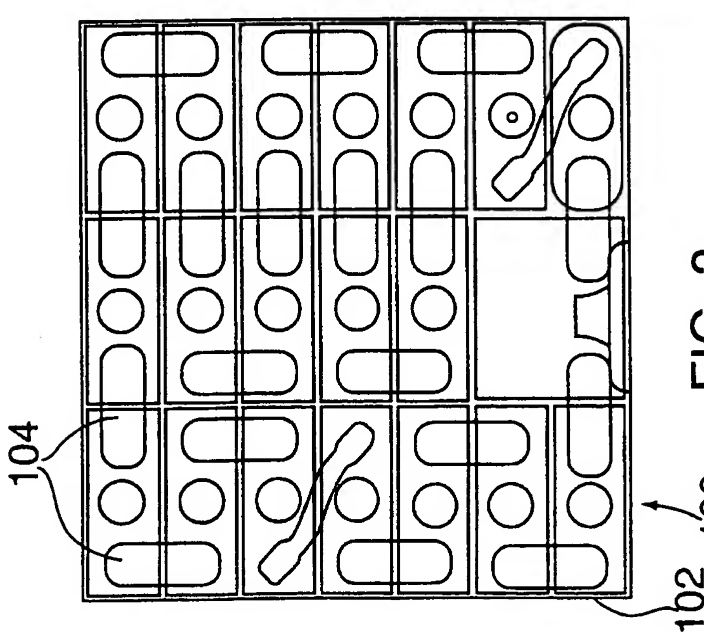

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/22866

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M10/48 H01M2/36 G01R31/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M G01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 937 528 A (PALANISAMY THIRUMALAI G) 26 June 1990 (1990-06-26) column 2, line 61 -column 3, line 68; claims 1,2,10 column 4, line 64 -column 7, line 4 column 8, line 36-54 column 13, line 50 -column 14, line 16; claims 1,2,10 ---	1,2,4,5, 7,8
X	US 5 281 919 A (PALANISAMY THIRUMALAI G) 25 January 1994 (1994-01-25)	1,2,7,8
A	column 4, line 31 -column 5, line 1 column 5, line 40 -column 9, line 57 column 14, line 61 -column 15, line 22; claims 1,2 ---	10,11

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 325 (E-368), 20 December 1985 (1985-12-20) & JP 60 157158 A (SHINKOUBE DENKI KK), 17 August 1985 (1985-08-17)	1,3,7
A	abstract	4,6
A	US 5 250 903 A (LIMUTI DONALD ET AL) 5 October 1993 (1993-10-05) claims 1-23	1-13
A	US 5 705 929 A (ROGNAS ROGER D ET AL) 6 January 1998 (1998-01-06) claims 1-32	1,7,13
A	US 5 049 803 A (PALANISAMY THIRUMALAI G) 17 September 1991 (1991-09-17) column 8, line 3-11 column 11, line 30-44 column 18, line 44 -column 22, line 38	1,4,7,10
A	GB 2 147 163 A (WEINLECHNER WOLFGANG) 1 May 1985 (1985-05-01) the whole document	13
A	FR 2 748 608 A (ACCUMULATEURS FIXES) 14 November 1997 (1997-11-14) page 4, line 15 -page 6, line 21	13
A	FR 2 020 290 A (GOULD NATIONAL BATTERIES INC) 10 July 1970 (1970-07-10) page 3, line 10 -page 5, line 28; claims 1-12	13

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/22866

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4937528 A	26-06-1990	DE 68924169 D	12-10-1995
		DE 68924169 T	21-03-1996
		EP 0438477 A	31-07-1991
		JP 2966870 B	25-10-1999
		JP 4502963 T	28-05-1992
		WO 9004188 A	19-04-1990
		US 4968942 A	06-11-1990
		US 5281919 A	25-01-1994
US 5281919 A	25-01-1994	US 4937528 A	26-06-1990
		DE 68924169 D	12-10-1995
		DE 68924169 T	21-03-1996
		EP 0438477 A	31-07-1991
		JP 2966870 B	25-10-1999
		JP 4502963 T	28-05-1992
		WO 9004188 A	19-04-1990
		US 4968942 A	06-11-1990
JP 60157158 A	17-08-1985	NONE	
US 5250903 A	05-10-1993	US 5132626 A	21-07-1992
		AU 5818790 A	07-01-1991
		EP 0431117 A	12-06-1991
		JP 4500431 T	23-01-1992
		WO 9015450 A	13-12-1990
US 5705929 A	06-01-1998	WO 9910854 A	04-03-1999
		EP 0934580 A	11-08-1999
US 5049803 A	17-09-1991	EP 0588790 A	30-03-1994
		WO 9222822 A	23-12-1992
		US 5160880 A	03-11-1992
GB 2147163 A	01-05-1985	DE 3332163 C	11-04-1985
		FR 2551585 A	08-03-1985
		JP 60072173 A	24-04-1985
FR 2748608 A	14-11-1997	NONE	
FR 2020290 A	10-07-1970	BE 739756 A	16-03-1970
		DE 1951018 A	27-08-1970
		JP 50012090 B	09-05-1975
		LU 59592 A	09-01-1970
		NL 6915416 A	14-04-1970

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